

# PATENT SPECIFICATION

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## (54) PRODUCTION OF POLYMERIC HYDROXY-CARBOXYLIC ACIDS

(71) We, DEUTSCHE GOLD-UND SILBER-SCHNEIDANSTALT VORMALS ROESSLER, a body corporate organised under the Laws of Germany of 9, Weiss-frauenstrasse, Frankfurt(Main), Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of polymeric hydroxycarboxylic acids containing a certain number of carboxyl or carboxylate groups on the one hand and hydroxyl groups on the other hand.

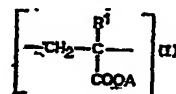
It is known that acrolein can be polymerised with the aid of free-radical catalysts to give C—C—polymers only interrupted to a limited extent by acetal bonds (*Makromolekulare Chemie* 53 (1962) pages 145 *et seq.*; 100 (1967), page 208).

It is also known that acrolein can be polymerised optionally in the presence of a monomeric vinyl compound in the presence of a catalyst and in the presence of H<sub>2</sub>O<sub>2</sub> in larger than catalytic quantities, resulting in the formation of polymers containing carboxyl groups (German Patent Specification 1,071,339). Polymers of this kind are suitable for the production of plastics and lacquers.

It is also known that polyacrolein can be reacted with formaldehyde in the presence of a strong base to give products which, in addition to the carboxyl groups, mainly contain alcohol groups (*Makromolekulare Chemie* 67 (1963) pages 186 *et seq.*; Belgian Patent Specification 611,797).

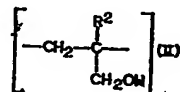
The present invention relates to a process for the production of solid linear or cross-linked polymers containing carboxyl or carboxylate groups and hydroxyl groups and optionally smaller numbers of lateral vinyl

or carbonyl groups, i.e. vinyl or carbonyl groups which are not situated in the main chain but project laterally therefrom, and, in the main chain, at least 75 mole per cent C—C bonds. The polymers are distinguished by the fact that they are composed predominantly of units of the general formulae:

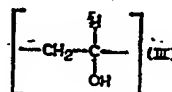


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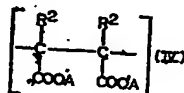
and



and/or



and optionally a number smaller than the sum of the numbers of units (I), (II) and (III) of units of the general formula:



in which

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A represents a hydrogen atom, a monovalent metal, preferably an alkali metal, more preferably sodium, a valence of a polyvalent metal, or ammonium,

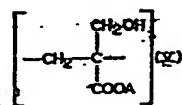
- 5 R<sup>2</sup> and R<sup>1</sup>, which may be the same or different, represent an alkyl group with from 1 to 6 carbon atoms, preferably a methyl group, or a hydrogen atom, in addition to which R<sup>1</sup> may represent a halogen atom, preferably a chlorine atom;

- 10 the units (I), (II), (III) and (IV) being arranged in any order, the average frequency of the units (I), (II), (III) and (IV) which, even in the absence of units (II), (III) and/or (IV), corresponds to a number ratio of carboxyl or carboxylate groups to hydroxyl groups of from 1.1 to 16, preferably from 2 to 9, and the polymers having a degree of polymerisation of at least 3, preferably from 3 to 5000 and more preferably from 3 to 600.

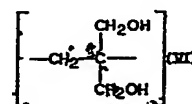
- The process according to the invention comprises subjecting acrolein to an oxidising polymerisation either alone or together with one or more co-monomers and subjecting the homo- or co-polymer formed to a Cannizzaro reaction with a strong base, preferably an alkali metal hydroxide.

- 25 The polymers produced according to the invention may be used with advantage as complex formers as is described in our co-pending application No. 4556/70 (Serial No. 1296412). They have the advantage over conventional complex formers which are usually compounds containing nitrogen, phosphorus or sulphur, that they do not create any problems in regard to effluent control, nor do they promote corrosion. They have the advantage over the polymers described in the Belgian Patent Specification referred to above that they form several times more stable complexes with metal ions, the complexes thus formed being much more readily soluble and also stable over a much wider pH range.

- 45 In the process according to the invention the polymers are prepared by polymerising acrolein under oxidising conditions and then treating the polymer with a strong base, preferably with an alkali metal hydroxide to perform the Cannizzaro reaction. In an alternative and less preferred embodiment, treatment with the strong base may also be accompanied by condensation with formaldehyde, in which case polymers are obtained which additionally contain units of the general formulae:



and



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in a number smaller than the sum of the number of units (I), (II), (III) and (IV).

In either case, however, the polymerisation and reaction conditions and especially the quantity in which the oxidising agent is used must be selected in such a way that the requisite ratio of carboxyl or carboxylate groups to the hydroxyl groups in the end product and the minimum degree of polymerisation 3 are maintained. Preferably the reaction conditions, especially the quantity of oxidising agent are selected in such a way as to produce polymers with an average degree of polymerisation of from 3 to 5000, more preferably 3 to 600, and a ratio of carboxyl or carboxylate groups to hydroxyl groups of from 2 to 9.

Peroxides of per acids may be used as oxidising agents, oxidation with H<sub>2</sub>O<sub>2</sub> being preferred. In polymerisation under oxidising conditions, the ratio of carboxyl groups to carbonyl groups can be adjusted in dependence upon the ratio between the quantity of oxidising agent and the quantity of acrolein. The greater this ratio, the larger will be the number of carboxyl groups present in the polymer and *vice versa*. Since the peroxidic compound also acts as a regulator, the degree of polymerisation is also governed by the quantities in which this compound is used. The degree of polymerisation decreases with increasing quantity of oxidising agent and *vice versa*. For example, an average degree of polymerisation of 3.2 and a COOH/CO ratio of 5:1 are obtained for an H<sub>2</sub>O<sub>2</sub>:acrolein molar ratio of 1:1. In by contrast a molar ratio of 0.7:1 is applied under otherwise the same conditions, these figures become 13 and 3.2:1, respectively.

Polymerisation of the acrolein under oxidising conditions may also be carried out in the presence of other copolymerisable monomers in almost any quantities. It is of particular advantage to use acrylic acid because it is possible in this way directly to influence the carboxyl group content of the polymer. In addition, the presence of acrylic acid in the starting mixture affects the degree of polymerisation in the sense that it increases with increasing acrylic acid content.

Examples of other copolymerisable monomers include alkyl acrylic acids, halogen-substituted acrylic acids, unsaturated polycarboxylic acids, especially maleic acid, and their derivatives such as esters and nitriles, also vinyl alcohol derivatives, allyl alcohols and derivatives thereof.

Depending upon the required carboxyl

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group content of the polymer, homopolymerisation or co-polymerisation of the acrolein may be carried out either as solution polymerisation or as precipitation polymerisation, preferably in aqueous medium. In cases where peroxidic compounds are used as oxidising agents, it is advisable initially to introduce these compounds and optionally the comonomer or a part thereof into aqueous solution or suspension and then to add the acrolein optionally together with the residual comonomer, advantageously at elevated temperatures of, for example, from 50 to 100°C. In the case of solution polymerisation, the polymers obtained may be directly used for further reaction, optionally after the solution has been concentrated. In this case, it is often favourable to destroy any residues of oxidising agent still present in the solution, for example by adding small quantities of  $MnO_2$  or active carbon. It is also possible, however, to precipitate the solution polymer from the reaction mixture with the aid of a dilute acid, for example hydrochloric acid. Residual monomers may be directly recovered from the reaction mixture, for example by distillation. In this case, the distillation residue is in the form of a highly concentrated aqueous solution of the polymer which may be used for further reaction. However, it is also possible to continue distillation to dryness in which case the pure polymer is obtained in solid form. In cases where polymerisation is carried out as precipitation polymerisation, the polymers may readily be separated by filtration. In this case, the residual monomers are present in the filtrate and can be used in this form. The precipitation polymers may be further purified with water, optionally with air bubbled through it.

The polyaldehyde carboxylic acids thus obtaining can be further reacted with a strong base, optionally in the presence of formaldehyde, in aqueous solution or suspension. The formaldehyde may be used in substantially stoichiometric quantities relative to the aldehyde groups present in the polymer, and stirred for a prolonged period at room temperature or at elevated temperatures of up to 100°C. After only 2 hours, the conversion is as high as 60 to 70%, rising to between 90 and 100% over a period of 24 hours. Under suitable conditions, the Cannizzaro reaction can, of course, also be carried out much more quickly, as applicable in particular to the reaction on the water-soluble polyaldehyde carboxylic acids. Where the reaction is carried out in solution, solutions are obtained which, in addition to the salts of the polyhydroxy carboxylic acids, contain an excess of alkali. They can be concentrated by evaporation to dryness. The salt obtained may be directly used as a complex former. The salts can be obtained in a particularly pure form by precipitating them from the reaction mixture, for example with methanol. It is also possible, however, to neutralise the solution before it is concentrated with a dilute acid, for example hydrochloric acid, or alternatively, to precipitate the free acid. Similarly, the Cannizzaro reaction may be displaced in such a way that ultimately substantially neutral salt solutions are obtained by measuring addition of the alkali in such a way that the excess of alkali gradually decreases as the reaction progresses, just reaching zero at the end of the reaction.

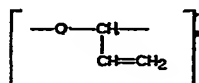
The excess of alkali is best only neutralised with acids of the kind whose salts do not give rise to any problems during application of the prepared polymers. Carbon dioxide, for example, may be used. However, it is of particular advantage to carry out neutralisation with the polyhydroxy carboxylic acids themselves in pure solid form or even directly with the reaction products from the first stage of the reaction, namely the polyaldehyde carboxylic acids or their solutions or suspension. It is possible in this way to obtain pure neutral solutions of the salts of the polyhydroxy carboxylic acids from which the acids themselves can readily be isolated by evaporating off the water. The polyhydroxy carboxylic acids which may be used for neutralisation may be, for example, precipitation polymers obtained as described above. They can readily be precipitated with a dilute acid from the solutions obtained on completion of the reaction.

The polymers produced according to the invention contain at least 75 mol per cent C—C bonds in the main chain and may be linear or cross-linked. The polymers are primarily synthesised from the aforementioned units (I) and (II) or (III). They represent the main constituent of the main chain synthesised from at least 75 mol per cent C—C bonds and to some extent are formed during treatment of the polyaldehydricarboxylic acid in a Cannizzaro reaction. However, this treatment may also be accompanied by intermolecular aldol condensations between the active CH groups in the  $\alpha$ -position to the aldehyde groups in the polyaldehyde carboxylic acid, and carbonyl groups of one or more adjacent chains. This gives rise to cross-linking. The aforementioned units (I), (II) and (III) are essential to the use of these polymers as complex formers.

In cases where other comonomers are used in addition to acrolein and optionally acrylic acid, for example maleic acid and/or vinyl alcohol derivatives and/or allyl alcohol, the units (III) and (IV) are still present in small numbers in the main chain in the polymer. They may be present in quantities of up to 50 mol %. Through them it is possible to control solubility in water and/or acidity and hence the usefulness of the complex formers even in extreme pH ranges.

In cases where the Cannizzaro reaction of the polyaldehyde carboxylic acids with a strong base is carried out in the presence of formaldehyde, the units (V) and (VI) are developed. The degree of crosslinking can be controlled in dependence upon the quantity of aldehyde used.

Although the polyaldehyde carboxylic acids are prepared by the radical polymerisation of acrolein, units corresponding to the formula:



may still be present in the main chains in small quantities of up to 25 mol %. In addition, small numbers of unchanged carbonyl groups may optionally be present in the end polymer. However, neither group is of any significance to the activity of the polymers as complex formers. Nor are the terminal groups present in the polymer, developed in dependence upon the reaction conditions and the reaction medium, of any significance in this respect. In cases where acrolein and  $\text{H}_2\text{O}_2$  are used as starting materials, one of the two terminal groups is always a hydroxyl group. In other cases, the terminal groups may be in the form of  $\text{COH---}$ ,  $\text{CH}_2\text{OH---}$ ,  $\text{COOH---}$  or  $\text{CH}_2=\text{CH---}$  groups or hydrogen atoms and residues of the catalyst used.

The polymers prepared according to the

$$\frac{\text{ml of calcium acetate solution} \times 25}{\text{weighed portion of complex former}} = \text{mg of bound CaCO}_3/\text{g of complex former}$$

The residual Hampshire value of the complex formers determined in this way is also a certain measure of the activity of these products as builders in detergents.

The complex stabilities quoted in the Examples were determined as follows:

1. Determination of complex stability with  $\text{Ca}^{++}$ : The concentration of free  $\text{Ca}^{++}$  in the complex forming equilibrium was measured by way of a complex between  $\text{Ca}^{++}$  and the metal indicator dye "Eriochromschwarz T", the complex stability constant being defined in accordance with:

$$K_{\text{stab}} = \frac{[\text{CaPODC}]}{[\text{Ca}^{++}][\text{PODC}^{-}]}$$

PODC<sup>-</sup> represents the anions of the complex formers taken as being polymeric hydroxy

invention have a minimum degree of polymerisation of 3. The upper limit is imposed solely by the purpose for which it is intended to use the polymers. For example, polymerisation degrees of around 5000 are possible.

As already mentioned, the polymers produced according to the invention may be used as complex formers in the broadest sense. They may be used anywhere where trace amounts of metals are undesirable, such as, for example, in detergents, rinsing agents, washing auxiliaries and cleaning agents, in the bleaching of wood and textiles, in the production of textiles and paper, in the preparation of pharmaceutical compositions and foodstuffs, in polymer chemistry, in metal working and processing and, in particular, in electrolysis baths.

The invention is illustrated by the following Examples. The Hampshire test quoted in the Examples is described in a handout published by Hampshire Chemical Corporation in June 1960, entitled "Hampshire NTA Technical Bulletin", Appendix, page A2. According to this publication, exactly 2 g of powdered complex former is dissolved in 50 ml of distilled water, neutralised, in 10 ml of a 2% sodium carbonate solution added, the pH value adjusted to between 11 and 12 and the solution diluted to 100 ml. It is then titrated with a calcium acetate solution containing 44.1 g of calcium acetate monohydrate per litre, until a distinct, permanent haze appears. The calcium carbonate binding capacity of the complex former may be calculated in accordance with the equation:

carboxylic acids. The measurements were taken in an

$\text{NH}_4\text{OH---NH}_4\text{Cl}$ -buffered

solution at pH 10.

2. Determination of complex stability with  $\text{Fe}^{+++}$ : By measuring the solubility product of  $\text{Fe}(\text{OH})_3$  in ammoniacal solution at pH 11, the complex stability constant being defined in accordance with:

$$K_{\text{stab}} = \frac{[\text{FePOC}^{++}]}{[\text{Fe}^{+++}][\text{POC}^{-}]}$$

POC<sup>-</sup> representing the anions of the complex formers taken as being polymeric hydroxy monocarboxylic acids.

3. Determination of complex stability with  $\text{Mn}^{++}$ ,  $\text{Cu}^{++}$ ,  $\text{Ag}^{+}$ : The metal ion concentration still free in the complex equi-

librium was measured by electron spin-resonance measurements; in the case of  $\text{Ag}^+$  by displacing the equilibrium of complex formation with  $\text{Mn}^{++}$  through the  $\text{Ag}^+$  ions that cannot be detected in the paramagnetic spin-resonance, the equilibrium constants being defined in accordance with:

$$K_{\text{Stab}}^{\text{Mn}^{++}} = \frac{[\text{MnPODC}]}{[\text{Mn}^{++}][\text{PODC}^{-}]}$$

$$K_{\text{stab}}^{\text{Cu}^{++}} = \frac{[\text{CuPODC}]}{[\text{Cu}^{++}][\text{PODC}^{-}]}$$

$$K_{\text{stab}}^{\text{Ag}^{+}} = \frac{[\text{AgPODC}]}{[\text{Ag}^{+}][\text{PODC}^{-}]}$$

$\text{PODC}^{-}$  being as defined in 1.

The percentage carboxyl and hydroxyl contents quoted relate to the number of  $\text{COOH}$ — and  $\text{OH}$ — groups per 100 monomer units (i.e.  $\text{C}_2$ -units in the chain) of the polymer molecule. All other percentages in the Example are by weight unless otherwise stated.

#### Example 1

a) 520 ml of distilled water and 260 ml of 30% hydrogen peroxide are heated to  $60^\circ\text{C}$ . 400 ml of freshly distilled acrolein are run in dropwise over a period of 2.5 hours at upwards of  $50^\circ\text{C}$ . White flaky polymer is precipitated during this period. After the acrolein has been added, the mixture is stirred for another 2 hours at  $60^\circ\text{C}$  under a gentle reflux which finally ceases altogether. It is then diluted with 500 ml of distilled water and, after another hour at  $60^\circ\text{C}$ , with another 500 ml of distilled water. The reaction mixture is left to cool and, after standing for a few hours, is filtered off, the precipitate washed free of odour with distilled water and dried *in vacuo* at  $50^\circ\text{C}$  over  $\text{NaOH}$ . 186 g of polyaldehyde carboxylic acid with an average molecular weight  $M=7500$  are obtained; degree of polymerisation P approximately 120; carboxyl content 44%; carbonyl content 27%.

b) 100 g of the polyaldehyde carboxylic acid prepared in accordance with Example 1a) are suspended in 400 ml of distilled water, followed by the addition of 100 ml of a 40% formaldehyde solution. 125 ml of a 40%  $\text{NaOH}$  are run into this mixture while stirring over a period of 40 minutes. 10 Minutes after the beginning of the  $\text{NaOH}$  addition, the reaction mixture becomes highly viscous and is diluted with 400 ml of distilled water. The addition of 60 ml of the prescribed quantity of  $\text{NaOH}$  produces a con-

siderable reduction in viscosity. A clear thinly liquid pale yellow solution is obtained. After standing for a few hours, the product is precipitated by running it in to 280 ml of a 20%  $\text{HCl}$ . The product is allowed to settle for 15 minutes, decanted off from the deposit and the deposit washed with distilled water. After predrying, pre-grinding, washing and drying to completion, 66 g of a polyhydroxy carboxylic acid with a carboxyl content of 58% and a hydroxyl content of 31% are obtained.

c) 3 g of the polyhydroxycarboxylic acid prepared in accordance with Example 1b) are suspended in 120 ml of distilled water, after which 15 ml of 1N sodium hydroxide are run in with stirring. A pH check carried out after 15 minutes shows a value of 7. The product is filtered off from any undissolved components and evaporated to dryness, giving 3.5 g of a polyhydroxycarboxylic acid- $\text{Na}$  salt whose complex stability with  $\text{Ca}^{++}$  is characterised by  $1 \text{ g } K_{\text{stab}}=0.34$  (measured at an ion strength  $I=0.23 \text{ mol l}^{-1}$ ). The product binds 300 mg of  $\text{CaCO}_3$  per gram of complex former (Hampshire test).

d) A polyhydroxycarboxylic acid solution prepared in accordance with Example 1b) and neutralised to pH 7 with 20% hydrochloric acid is evaporated to dryness, giving approximately 150 g of a salt mixture of which about 85% consists of polyhydroxy carboxylic acid- $\text{Na}$  salt and 15% of  $\text{NaCl}$ . The stability constant of the complex of this salt mixture (calculated for 100% of polyhydroxycarboxylic acid- $\text{Na}$  salt) amounts to:  $1 \text{ g } K_{\text{stab}}=1.90$  with  $\text{Ca}^{++}$  (at an ion strength  $I=0.24 \text{ mol l}^{-1}$ ). The Hampshire value is 325.

#### Example 2

The polymerisation under oxidising conditions of  $\alpha$ -ethylacrolein as in the preceding Example again gives a polyaldehyde carboxylic acid which can be directly converted by a subsequent Cannizzaro reaction in an aqueous suspension with alkali metal hydroxide into the complex former in the form of a polyhydroxycarboxylic acid salt with a  $\text{COOH}$  content of 50% and an  $\text{OH}$  content of 21%. The product shows, for example, a complex stability of the complexes with  $\text{Ca}^{++}$  characterised by:  $1 \text{ g } K_{\text{stab}}=2.55$  (measured at an ion strength  $I=0.24 \text{ mol l}^{-1}$ ).

The Hampshire value is 180; the complex stability of the complex with  $\text{Fe}^{+++}$  is characterised by  $1 \text{ g } K_{\text{stab}}=29.6$  (based on ion strength  $I=1.0 \text{ mol l}^{-1}$ ); in addition the product shows outstanding surface active properties.

#### Example 3

a) A mixture of 500 ml of distilled water and 500 ml of 30%  $\text{H}_2\text{O}_2$  is heated with a

heating bath (60°C) to a temperature of 50°C. 300 ml of acrolein are run in dropwise with vigorous stirring over a period of 4 hours under a gentle reflux, producing a rise in the reaction temperature to 65°C. After the acrolein has been added, the mixture is stirred for another 2½ hours at that temperature and then left to cool. After standing for a few hours, 0.025 g of MnO<sub>2</sub> are added and the reaction mixture concentrated to half its volume. A highly viscous clear distillation residue (A) is obtained.

10% of the distillation residue (A) is dried *in vacuo* for the purposes of analysis and determining the yield. 8.7 g of a pure solid polymer are obtained. Average molecular weight  $M=1800$ ; degree of polymerisation approximately 28; carboxyl content 59%; carbonyl content 21%.

b) 500 ml of the distillation residue (A) are diluted with 500 ml of distilled water. This solution is added dropwise with 250 ml of a 40% NaOH solution to 250 ml of stirred 40% formaldehyde. The dropping rate is selected in such a way that the reaction temperature remains below 40°C. 30 minutes after the addition, another 60 ml of 40% NaOH are added to the reaction mixture. After 20 ml of NaOH have been added, the reaction solution changes colour from colourless to dark reddish brown (pH 7.2) and, after 60 ml have been added, from dark reddish brown to pale yellow (pH 11.5), indicating the addition of the quantity of NaOH required for the reaction.

c) After the polyhydroxycarboxylic acid prepared in accordance with Example 3b) has been precipitated with dilute HCl, washed free from chloride residues and treated with the stoichiometric quantity of alkali, a complex former solution is obtained from which the pure solid complex former can readily be obtained.

The following are examples of the complex forming activity of this product:

Complex forming with Ca<sup>++</sup>:

1g  $K_{stab}=2.16$  (measured at ion strength  $I=0.24$  mol l<sup>-1</sup>) Hampshire value 400.

#### Example 4

a) 430 ml of a distillate of the kind obtained during recovery of residual monomers (cf. Example 11) and consisting of approximately 7% acrylic acid, 1% of acrolein and 92% of water, are introduced into a reaction vessel together with 400 ml of 30% H<sub>2</sub>O<sub>2</sub>. 365 ml of freshly distilled acrolein are added dropwise to the reaction mixture at upwards of 55°C over a period of some 5 hours during which the mixture is stirred and heated with a heating bath (60°C). After the acrolein has been added, the mixture is

briefly heated to around 80°C, left to cool, concentrated to around half its volume and immediately used in the form of a solution of a polyaldehyde carboxylic acid (COOH

content=80%, CO content 20%,  $\bar{P}=10$ ).

b) 2/5 (i.e. 200 ml) of the polyaldehyde carboxylic acid solution prepared in Example 4a) is mixed with 272 ml of distilled water. 175 ml of 40% concentrated NaOH are then run in dropwise while stirring over a period of 1.5 hours. After standing for a few hours, an alkaline solution of a salt of a polyhydroxycarboxylic acid is obtained, the completed complex former solution being obtained following neutralisation with a little similarly prepared solid polyhydroxycarboxylic acid (for example in accordance with Example 3b). The product, which can readily be obtained from the complex former solution by evaporating off the water, forms, for example, complexes with Ca<sup>++</sup> ions characterised by 1g  $K_{stab}=1.9$  (measured at ion strength  $I=0.24$  mol l<sup>-1</sup>), Hampshire value 325.

#### Example 5

a) 500 ml of distilled water and 125 ml of H<sub>2</sub>O<sub>2</sub> are heated while stirring to 55°C, and a mixture of 125 ml of freshly distilled acrolein and 380 ml of freshly distilled acrylic acid added dropwise over a period of 4 hours at upwards of 55°C. After the acrolein and acrylic acid have been added, the reaction mixture solidifies into a gel and is diluted with 1150 ml of distilled water. After standing for a few hours, the gel-like product is converted by drying *in vacuo* over NaOH at 75°C into a pure solid polymer. 320 g of polyaldehyde carboxylic acid (COOH content 80%, carbonyl content 12%,

$\bar{P}=320$ ) are obtained.

b) 250 g of a polyaldehyde carboxylic acid of the kind obtained, for example, in accordance with Example 5a) are suspended in 750 ml of distilled water, the resulting suspension mixed with 125 ml of 40% formaldehyde and then 325 ml of a 30% NaOH solution are added dropwise with stirring over a period of some 3 hours. After standing for a few hours, 1/5 of the mixture is precipitated with dilute HCl, washed and dried in order to identify the polyhydroxycarboxylic acid formed. A product with a COOH content of 62.8% and an OH content of 13.5% is obtained.

c) The remaining 4/5 of the mixture are neutralised with 8 g of solid polyhydroxycarboxylic acid obtainable, for example, by one of any of the processes described above. A pure aqueous complex former solution is obtained in this way. Pure solid complex former is obtained by evaporation, its activity being as follows:

	Complex Formation With	Characterised by:	
5	$\text{Ca}^{++}$	1g $K_{stab}=2.2$ (measured at ion strength $I=0.24 \text{ mol l}^{-1}$ )	are obtained after precipitation with 225 ml 60 of a 10% HCl, washing and drying.
	$\text{Fe}^{+++}$	1g $K_{stab}=31.2$ (measured at pH=12.1; based on ion strength $I=1.0 \text{ mol l}^{-1}$ )	b) The salt of this polyhydroxycarboxylic acid prepared as described above forms complexes with metal ions (1g $K_{Fe^{++}}=27.5$ , based on an ion strength $I=1.0 \text{ mol l}^{-1}$ ; 65 Hampshire value 111).
10	$\text{Mg}^{++}$	absence of precipitability with: $\text{OH}^-$ , $\text{CO}_3^{--}$ , $\text{F}^-$	Example 8 Reaction of a polyaldehyde carboxylic acid
	$\text{Ba}^{++}$	absence of precipitability with: $\text{CO}_3^{--}$ , oxalate $^{--}$	$\bar{P}=3.2$ ; COOH content=67%; CO content=14% prepared, for example, in accordance with one of the methods described above, with formaldehyde and KOH gives a complex former in the form of the potassium salt of the polyhydroxycarboxylic acid whose activity is shown, for example, by its complex formation with $\text{Ca}^{++}$ : 1g $K_{stab}=1.61$ (measured at an ion strength $I=0.24 \text{ mol l}^{-1}$ , Hampshire value 245. 75
15	$\text{La}^{+++}$	absence of precipitability with: oxalate $^{--}$ , $\text{CO}_3^{--}$ , $\text{PO}_4^{3-}$	Example 9
	$\text{Cr}^{+++}$	absence of precipitability with: $\text{PO}_4^{3-}$	a) A mixture of 430 ml of a distillate from the recovery of residual monomers (1% of acrolein, 7% of acrylic acid, 92% of water) and 400 ml of 35% $\text{H}_2\text{O}_2$ is introduced into a reaction vessel. 365 ml of freshly distilled acrolein are added dropwise with stirring over a period of 4 hours during which time the mixture is heated in a heating bath at 60°C. The reaction temperature is kept at 65°C by gentle cooling. After the acrolein has been added, 3.0 g of benzoyl peroxide are added, stirring continued for another 3 hours at 65°C, 0.04 g of $\text{MnO}_2$ added and the product left to cool slowly. It is then concentrated to a volume of around 600 ml. An approximately 63% concentrated polyaldehyde carboxylic acid solution is obtained (COOH content=68%, CO content=20%, $\bar{P}=9$ ). 80
20	$\text{Co}^{++}$	absence of precipitability with: $\text{OH}^-$ , $\text{CO}_3^{--}$ , $\text{PO}_4^{3-}$	85
	$\text{Ni}^{++}$	absence of precipitability with: $\text{PO}_4^{3-}$ , $\text{OH}^-$ , $\text{CO}_3^{--}$	85
25	$\text{Zn}^{++}$	absence of precipitability with: $\text{CO}_3^{--}$	85
	$\text{Cd}^{++}$	absence of precipitability with: oxalate $^{--}$ , $\text{OH}^-$ , $\text{CO}_3^{--}$	85
30	$\text{Ti}^{+}$	absence of precipitability with: $\text{BrO}_3^-$	85
	$\text{Pb}^{++}$	absence of precipitability with: $\text{SO}_4^{--}$ , $\text{OH}^-$ in strongly alkaline solution also $\text{CO}_3^{--}$	85
35	Example 6 Following conversion in a Cannizzaro reaction accompanied by condensation with formaldehyde, a polyaldehyde carboxylic acid		85
		$\bar{P}=600$ , COOH content=56%, CO content=9% obtained by copolymerisation under oxidising conditions of acrolein with acrylic acid in the presence of hydrogen peroxide by the methods described above gives a complex former in the form of a salt of a polyhydroxycarboxylic acid (COOH content=54%, OH content=10%), whose complex forming activity is characterised, for example, by complex forming with $\text{Ca}^{++}$ : 1g $K_{stab}=2.12$ (measured at an ion strength $I=0.24 \text{ mol l}^{-1}$ ); complex forming with $\text{Fe}^{+++}$ : 1g $K_{stab}=29.3$ (based on an ion strength $I=1.0 \text{ mol l}^{-1}$ ). Hampshire value 306. 90	90
40			95
45			100
50			105
	Example 7 a) 20 g of a polyaldehyde carboxylic acid (COOH content=41%, CO content=9%, $\bar{P}=150$ ) are suspended in 200 ml of distilled water, 20 ml of a 40% HCHO solution added followed by the gradual addition with stirring of 50 ml of a 40% NaOH. Another 50 ml of a 40% HCHO solution are then added, followed by stirring for 1 hour at room temperature. 18 g of polyhydroxycarboxylic acid (COOH content=64%, OH content=11%)		110
55			115
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maximum reaction temperature scarcely exceeds 60°C. After standing for a few hours, the excess  $H_2O_2$  is eliminated again with  $MnO_2$ , after which the polyaldehyde carboxylic acid can be obtained in pure form. 296 g of product obtained, COOH content=77%, carbonyl content=15%,  $\bar{P}=3$ .

b) Reaction of the product of Example 10a) with alkali metal hydroxide in the presence of formaldehyde, followed by neutralisation of the alkaline complex former solution after the Cannizzaro reaction with solid polyhydroxycarboxylic acid, gives an approximately 40% aqueous complex former solution. The product forms, for example:

Water-soluble Complexes with:

Characterised by:

- 20  $Ca^{++}$  1g  $K_{stab}=2.06$  (measured at ion strength  $I=0.24$  mol  $l^{-1}$ )  
 $Fe^{+++}$  1g  $K_{stab}=29.4$  (measured at  $pH=11.7$ ; based on ion strength  $I=1.0$  mol  $l^{-1}$ )  
 25  $Mg^{++}$  absence of precipitability with:  $OH^-$ ,  $CO_3^{--}$ ,  $F^-$   
 $Ba^{++}$  absence of precipitability with:  $CO_3^{--}$ , oxalate $^{--}$   
 $La^{+++}$  absence of precipitability with: oxalate $^{--}$ ,  $CO_3^{--}$ ,  $PO_4^{3-}$   
 30  $Cr^{+++}$  absence of precipitability with:  $PO_4^{3-}$   
 $Co^{++}$  absence of precipitability with:  $OH^-$ ,  $CO_3^{--}$ ,  $PO_4^{3-}$   
 35  $Ni^{++}$  absence of precipitability with:  $PO_4^{3-}$ ,  $OH^-$ ,  $CO_3^{--}$   
 $Zn^{++}$  absence of precipitability with:  $CO_3^{--}$   
 $Cd^{++}$  absence of precipitability with: oxalate $^{--}$ ,  $OH^-$ ,  $CO_3^{--}$   
 40  $Tl^+$  absence of precipitability with:  $BrO_3^-$   
 $Pb^{++}$  absence of precipitability with:  $SO_4^{--}$ ,  $OH^-$  in strong alkaline solution also  $CO_3^{--}$   
 45

#### Example 11

a) 350 ml of freshly distilled acrolein are run with stirring over a period of 2.2 hours into a mixture heated to 55°C of 350 ml of distilled water and 500 ml of 30%  $H_2O_2$ . The reaction temperature rises to 65°C, reaching 70°C one hour after the acrolein has been added. Another 25 ml of a 30%  $H_2O_2$  are then added. After another hour, the temperature of the reaction mixture has risen to 80°C. The mixture is then cooled to 50°C, any unreacted  $H_2O_2$  left is destroyed with 50 mg of  $MnO_2$  and, after stirring for about 1 hour at 50°C, the product is concentrated *in vacuo* to around half the liquid volume. A distillate is obtained which contains 7% of

acrylic acid and approximately 1% of acrolein in water and which can be used again immediately for the next batch. 10% of the polymer solution obtained are evaporated to dryness for the purpose of analysis and determining the yield, the rest is used for further reaction. A total (based on the total yield) of 250 g of polyaldehyde carboxylic acid is obtained (COOH content=72%, carbonyl content=14%,  $\bar{P}=5$ ).

b) 80 ml of a 40% formaldehyde solution are added to 450 ml of the polymer solution thus prepared, followed by the dropwise addition with stirring over a period of 45 minutes of 211 ml of a 40% concentrated NaOH. The reaction mixture is slightly cooled to keep the reaction temperature below 70°C. After the NaOH has been added, the mixture is stirred for 1 hour until the reaction temperature has fallen to 30°C. Another 320 ml of a 40% NaOH are then slowly added. After standing for a few hours, the product is neutralised with 51 g of a polyhydroxycarboxylic acid, water evaporated off and the residue dried. 480 g of polyhydroxycarboxylic acid salt are obtained (1g  $K_{Ca^{++}}=1.54$  measured at an ion strength  $I=0.24$  mol  $l^{-1}$ ; Hampshire value 320).

#### Example 12

a) 500 ml of distilled water and 250 ml of a 30%  $H_2O_2$  are mixed together and heated while stirring at 55°C. A mixture of 220 ml of acrolein and 205 ml of acrylic acid (both freshly distilled) is added dropwise at upwards of 55°C. The dropwise addition is over after 3.75 hours. Stirring is continued at 60°C for another hour at the end of which the temperature of the reaction mixture has spontaneously risen to 65°C to form a viscous polymer foam. The product is diluted with 1 litre of distilled water, thoroughly stirred and left to react for a few hours at room temperature. It is then diluted with another 500 ml of distilled water, the thixotropic gel converted by vigorous stirring into a low viscosity liquid, excess hydrogen peroxide destroyed by adding 0.25 g of active carbon and heating to 56°C and finally the pure solid polymer obtained by evaporating off the water followed by drying. 279 g of polyaldehyde carboxylic acid are obtained (COOH content 71%, carbonyl content 22%,  $\bar{P}=60$ ).

b) 1100 ml of a gel prepared in accordance with Example 12a) with a solids content of 237 g are diluted with 240 ml of distilled water following destruction of the excess hydrogen peroxide, after which 107 ml of 40% formaldehyde solution are added and finally 443 ml of 40% concentrated NaOH run in while stirring over a period



of some 4 hours. After standing for a few hours, another 20 ml of 40% concentrated NaOH are added, the product left standing for a few hours and filtered.

- 5 c) 4/5 of this alkaline polyhydroxycarboxylic acid-Na salt solution are neutralised with 8 g of solid polyhydroxycarboxylic acid (for example prepared in accordance with one of the preceding Examples), and filtered  
10 off from any undissolved components.

A 21% solution of the complex former is obtained which may either be directly used as in all the other Examples or from which the complex former can be obtained in pure solid form by evaporating off the water. (For  
15 example, complex stability with  $\text{Ca}^{++}$  ions:  $1\text{g } K_{stab}=2.06$  measured at an ion strength  $I=0.24 \text{ mol l}^{-1}$ ; Hampshire value 377).

#### Example 13

- 20 a) A product obtained as in Example 14 by the copolymerisation under oxidising conditions of acrolein with acrylic acid and maleic acid (mixture: 50 mol % of acrylic acid and 10 mol % of maleic acid relative  
25 to the quantity of acrolein; 10 mol % of acrolein excess relative to the quantity of  $\text{H}_2\text{O}_2$ ), with an average degree of polymerisa-

tion  $\bar{P}=65$ , COOH content 70%, CO content 20%, obtained in a yield of approximately 75% of the theoretical, is again subjected to the Cannizzaro reaction.

- b) 400 ml of this (approximately 40% concentrated) polymer solution are mixed with 233 ml of distilled water. 440 ml of 20%  
35 concentrated NaOH are then gradually added dropwise with stirring, and finally the pH value adjusted to pH 11. After standing for a few hours, a pH value of 9.5 prevails in the reaction mixture. The mixture is then  
40 neutralised again to pH 7, immediately giving an approximately 25% concentrated complex former solution.

Complex forming with  $\text{Ca}^{++}$ :  $1\text{g } K_{stab}=2.05$  (measured at ion strength  $I=0.24 \text{ mol l}^{-1}$ ;  
45 Hampshire value 360).

Complex formation with  $\text{Fe}^{+++}$ :  $1\text{g } K_{stab}=29.0$  (based on ion strength  $I=1.0 \text{ mol l}^{-1}$ ).

#### Example 14

- 50 a) 700 ml of acrolein are run in dropwise with stirring over a period of some 4.3 hours at upwards of  $50^\circ\text{C}$  to a solution of 225 g of maleic acid anhydride in 400 ml of distilled water+800 ml of 30%  $\text{H}_2\text{O}_2$  at heating bath temperature of  $60^\circ\text{C}$ . After standing  
55 for a few hours, the product is filtered off from the precipitation polymer deposited, giving a polyaldehyde carboxylic acid with a COOH content of 46%, a CO content of

43%,  $\bar{P}=90$  (22 mol % of maleic acid units). The filtrate is an aqueous solution of a low molecular weight polyaldehyde car-

boxylic acid of similar structure and may be similarly used for the preparation of complex former.

- b) 50 g of polyaldehyde carboxylic acid  
65 prepared in accordance with Example 14a) are suspended in 38 ml of distilled water+50 ml of 40% formaldehyde, 65 ml of 40% concentrated NaOH gradually being added dropwise with stirring to the resulting suspension. After the alkali has been added, the mixture is left standing for a few hours, after which it is neutralised with freshly precipitated polyhydroxycarboxylic acid prepared in accordance with one of the preceding  
75 Examples still moist after being washed free from acid. After the product has been filtered off from any undissolved components, an aqueous complex former solution is obtained. The complex former is characterised, for  
80 example, by the following:

Complex forming with  $\text{Ca}^{++}$ :

$1\text{g } K_{stab}=1.52$  (measured at ion strength  $I=0.25 \text{ mol l}^{-1}$ ); Hampshire value 224.  
85

Complex forming with  $\text{Fe}^{+++}$ :

$1\text{g } K_{stab}=29.6$  (based on ion strength  $I=1.0 \text{ mol l}^{-1}$ ).

#### Example 15

- a) 110 ml of distilled water are introduced  
90 into a reaction vessel with 270 ml of 30%  $\text{H}_2\text{O}_2$  and heated to  $50^\circ\text{C}$  with a heating bath ( $50^\circ\text{C}$ ). A mixture of 200 ml of freshly distilled acrolein and 216 ml of freshly distilled acrylic acid is run in with continuous stirring over a period of 75 minutes. The reaction temperature rises to  $65^\circ\text{C}$ , reaching  
95  $100^\circ\text{C}$  15 minutes after the acrolein and acrylic acid have been added, still with a gentle reflux. The reaction mixture is cooled to a temperature of  $30^\circ\text{C}$  by the addition of 1000 ml of distilled water and external cooling, whilst any polymer flakes that have been precipitated under heat are gradually redissolved. The reaction mixture is then left  
100 standing for a few hours, solidifying into a highly viscous slightly opalescent solution. It is then diluted with 500 ml of distilled water and precipitated while stirring with 300 ml of a 20% hydrochloric acid. The white cheese-  
105 like deposit is left to settle for approximately 1 hour, after which it is filtered, washed free from acid with distilled water and dried *in vacuo* over NaOH at a temperature of  $60^\circ\text{C}$ . 187 g of a polyaldehyde carboxylic acid with an average molecular weight  $M=8100$  are obtained; degree of polymerisation approximately 120; carboxyl content 69%; carbonyl content 26%.

- b) 166 g of the polyaldehyde carboxylic  
120 acid obtained in Example 15a) are suspended in 500 ml of distilled water, after which 800 ml of a 40% formaldehyde solution and

166 ml of a 40% NaOH solution are run in over a period of 40 minutes. After the clear pale yellow solution has been filtered off from a few undissolved components, it is left standing for a few hours and then neutralised by the addition of solid polyhydroxycarboxylic acid (prepared in accordance with Example 3) in 2 g portions. After a total of 12.3 g of polyhydroxycarboxylic acid has been dissolved, the pH value of the reaction solu-

tion reaches a level between 5 and 6. The solution is filtered off from the few undissolved components and evaporated to dryness.

Drying of the solid salt *in vacuo* at 110°C gives 175 g of solid polyhydroxycarboxylic acid-Na salt with a complex stability with Ca<sup>++</sup> ions characterised by: 1g K<sub>stab</sub>=2.05 (measured at an ion strength I=0.23 mol l<sup>-1</sup>) and a Hampshire value of 500;

with Fe<sup>+++</sup>: 1g K<sub>stab</sub>=29.1 (pH=11.5; I=1.0 mol l<sup>-1</sup>)

with Mn<sup>++</sup>: 1g K<sub>stab</sub>=4.5 (pH=9.4; I=0.1 mol l<sup>-1</sup>)

with Ca<sup>++</sup>: 1g K<sub>stab</sub>=2.7 (pH=9.7; I=0.25 mol l<sup>-1</sup>)

with Ag<sup>+</sup> 1g K<sub>stab</sub>=3.7 (pH=7.0; I=0.0025 mol l<sup>-1</sup>).

In the presence of the complex former in a concentration of 1 mol l<sup>-1</sup>, the solubility product of AgCl is not exceeded, for example, from a 5.10<sup>-4</sup> molar Ag<sup>+</sup> solution with Cl<sup>-</sup> ions in concentration of up to 10<sup>-3</sup> mol l<sup>-1</sup>. Therefore, even in the most unfavourable case that no oversaturation effects should occur, no more AgCl is precipitated.

#### Example 16

a) 1529 ml of an aqueous stabiliser-free crude acrolein solution (containing approximately 25% of acrolein) are added dropwise with stirring at a rate of 10 ml per minute to 660 ml of a 30% H<sub>2</sub>O<sub>2</sub> heated in a heating bath (60°C). Following the addition of 0.08 g of MnO<sub>2</sub>, the product is concentrated to around 1100 ml. An approximately 40% concentrated polyaldehyde carboxylic acid solution (COOH content 68%, CO content 20%,

hydroquinone-stabilised aqueous crude acrolein solution gives a polyaldehyde carboxylic acid solution (COOH content 80%, CO content 20%,

P=18, based on the pure solid polymer) which after the Cannizzaro reaction in accordance with Example 16b) leads to a polyhydroxycarboxylic acid salt solution (COOH content 58%, OH content 7%, based on the pure solid polymer). The product again shows complex forming activity with metal ions as demonstrated, for example, by the following (based on the activity of the pure solid polyhydroxycarboxylic acid-Na salt):

Complex forming with Ca<sup>++</sup>:

1g K<sub>stab</sub>=1.83 (measured at ion strength I=0.24 mol l<sup>-1</sup>); Hampshire value 326.

Complex forming with Fe<sup>+++</sup>:

1g K<sub>stab</sub>=30.2.

P=9) is obtained.

b) 600 ml of this polymer solution are diluted with 380 ml of distilled water. The pH value is adjusted to 12 by the addition with stirring of 20% concentrated NaOH (at a rate of 10 ml per minute). After standing for a few hours, the solution is neutralised. The complex former thus prepared is characterised, for example, in its activity by the following (based on the pure solid product):

Complex forming with Ca<sup>++</sup>:

1g K<sub>stab</sub>=1.45 (measured at an ion strength I=0.24 mol l<sup>-1</sup>); Hampshire value 356).

Complex formation with Fe<sup>+++</sup>:

1g K<sub>stab</sub>=28.5 (based on ion strength I=1.0 mol l<sup>-1</sup>).

#### Example 17

The procedure of Example 16a) using

#### Example 18

a) A mixture of 580 ml of freshly distilled acrolein and 117 ml of distilled acrylic acid is added dropwise (at a rate of 3.0 ml per minute) to a stirred mixture of 800 ml of 30% H<sub>2</sub>O<sub>2</sub> and 400 ml of distilled water heated with a heating bath. On completion of the reaction, highly viscous approximately 34% concentrated polyaldehyde carboxylic acid solution is obtained (COOH content

75%, CO content 21%, P=10, based on the pure solid polymer).

b) 405 ml of 20% concentrated NaOH are gradually added with stirring to 500 ml of this polymer solution. After standing for a few hours, the product is precipitated with methanol. After the deposit has been briefly dried *in vacuo* at 100°C, pure solid polyhydroxycarboxylic acid-Na salt is obtained, its complex forming capacity being illustrated, for example, by the following:

Complex formation with  $\text{Ca}^{++}$ :

$1g K_{stab}=1.8$  (measured at ion strength  $I=0.24 \text{ mol l}^{-1}$ ); Hampshire value 334.

Complex formation with  $\text{Fe}^{+++}$ :

$1g K_{stab}=28.5$ .

#### Example 19

a) A mixture of 945 ml of distilled water, 307 ml of freshly distilled acrolein and 168 ml of freshly distilled acrylic acid is heated to  $55^\circ\text{C}$ . 105 ml of a 30%  $\text{H}_2\text{O}_2$  solution is then run in with vigorous stirring over a period of 1.5 hours at upwards of this temperature. The product is then diluted with 200 ml of distilled water and the temperature gradually increased to  $70^\circ\text{C}$ . After the temperature of the reaction mixture has risen to  $75^\circ\text{C}$  through the heat of reaction, the product is diluted with 200 ml of distilled water and cooled to  $50^\circ\text{C}$ . It is then precipitated with 200 ml of a 10%  $\text{HCl}$ , left briefly to settle and then filtered. After the polymer has been washed and dried, 165 g of polyaldehyde carboxylic acid are obtained (COOH content 58%, carbonyl content 6%,  $\bar{P}=110$ ).

b) 100 g of this polyaldehyde carboxylic acid are suspended in 300 ml of distilled water and 50 ml of a 40%  $\text{HCHO}$  solution added to the resulting suspension. 87 ml of a 40%  $\text{NaOH}$  solution are then slowly run in with stirring. After 50 minutes stirring, the reaction mixture reacts neutrally. Another 43 ml of a 40%  $\text{NaOH}$  solution are added, and the product is left standing for one hour. This is followed by precipitation with 231 ml of a 20%  $\text{HCl}$  solution. After washing and drying, 89 g of polyhydroxycarboxylic acid are obtained (COOH content 73%, OH content 8%).

c) Treatment of the polyhydroxycarboxylic acid with  $\text{NaOH}$  again gives the readily water-soluble salt which as a complex former is characterised by:  $1g K_{Ca^{++}}=1.82$ ; Hampshire value 332.

#### Example 20

a) 813 ml of acrolein are added dropwise over a period of some  $4\frac{1}{2}$  hours at upwards of  $50^\circ\text{C}$  to a stirred mixture (in a heating bath at  $60^\circ\text{C}$ ) of 800 ml of 30%  $\text{H}_2\text{O}_2$  and 400 ml of a distillate of the kind obtained during recovery of residual monomers consisting of 1% acrolein, 7% of acrylic acid and 92% of water. The reaction temperature gradually rises to around  $80^\circ\text{C}$ , falling slowly again after passing this maximum. After standing for a few hours, the product is precipitated with 500 ml of 20%  $\text{HCl}$ , the deposit filtered off, washed and dried. A polyaldehyde carboxylic acid with an average

degree of polymerisation  $\bar{P}=79$ , a carboxyl content of 61% and a carbonyl content of 4% is obtained.

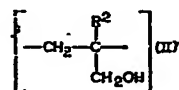
b) Reaction of this product in a Cannizzaro reaction accompanied by condensation with formaldehyde by the methods described above leads to a polyhydroxycarboxylic acid with a carboxyl content of 64% and a hydroxyl content of 4%. In the form of its salts, the product is again suitable for use as a complex former (for example, complex formation with  $\text{Ca}^{++}$ :  $1g K_{stab}=1.58$  measured at ion strength  $I=0.24 \text{ mol l}^{-1}$ ; Hampshire value 202).

#### WHAT WE CLAIM IS:—

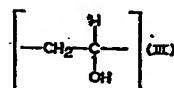
1. A process for the production of solid linear or cross-linked polymers containing at least 75 mol per cent C—C bonds in the main chain and composed predominantly of units of the general formulae:



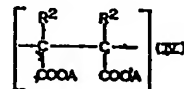
and



and/or



and optionally a number smaller than the sum of the number of units (I), (II), and (III) of units of the general formula:



in which

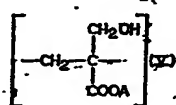
A represents a hydrogen atom, a monovalent metal, a valence of a polyvalent metal or ammonium,

$\text{R}^2$  and  $\text{R}^1$ , which may be the same or different, represent an alkyl group with from 1 to 6 carbon atoms or a hydrogen atom, in addition to which  $\text{R}^1$  may also represent a halogen atom,

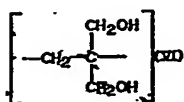
the units (I), (II), (III) and (IV) being arranged in any order, the number ratio of carboxyl or carboxylate groups to hydroxyl groups being from 1.1 to 16, and the poly-

- 5 mers having a degree of polymerisation of at least 3, which process comprises subjecting acrolein to an oxidising polymerisation either alone or together with one or more co-monomers and subjecting the homo- or co-polymer  
10 formed to a Cannizzaro reaction with a strong base.

2. A process as claimed in Claim 1, in which the Cannizzaro reaction is carried out in the presence of formaldehyde to produce  
15 a polymer containing units of the general formulae:



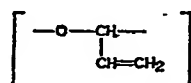
and



- 20 in a number smaller than the sum of the number of units (I), (II), (III) and (IV).

3. A process as claimed in Claim 1 or 2, wherein the strong base is an alkali metal hydroxide.

- 25 4. A process as claimed in any of Claims 1 to 3, wherein the polymer formed contains up to 25 mol % of units corresponding to the formula:



5. A process as claimed in any of claims 1 to 4, wherein the acrolein is subjected to an oxidising polymerisation in the presence of at least one co-monomer which is acrylic acid, an alkyl acrylic acid, a halogen-substituted acrylic acid or an unsaturated polycarboxylic acid.  
35

6. A process as claimed in Claim 5, wherein the unsaturated polycarboxylic acid is maleic acid.

7. A process as claimed in any of Claims 1 to 6, wherein polymerisation conditions are selected to produce a polymer with a degree of polymerisation of from 3 to 5000.  
40

8. A process as claimed in any of Claims 1 to 7, wherein polymerisation conditions are selected to produce a polymer in which the ratio of carboxyl or carboxylate groups to hydroxyl groups is from 2 to 9.  
45

9. A process as claimed in any of Claims 1 to 8, wherein polymerisation conditions are selected to produce a polymer with a degree of polymerisation of from 3 to 600.  
50

10. A process as claimed in any of Claims 1 to 9, wherein R<sup>1</sup> and/or R<sup>2</sup> is a methyl group or a hydrogen atom.  
55

11. A process for the production of a polymer containing carboxyl or carboxylate groups and hydroxyl groups, substantially as hereinbefore described with reference to any of the Examples.  
60

12. A polymer when produced by a process as claimed in any of Claims 1 to 11.

ELKINGTON & FIFE,  
Chartered Patent Agents,  
High Holborn House,  
52/54 High Holborn,  
London, WC1V 6SH.  
Agents for the Applicants.